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HIGHLIGHTS FROM RECENT LITERATURE

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Each issue of *Gold Bulletin* contains key highlights from the research and patent literature. Authors who publish high quality work in other journals are invited to send a copy of their publication to the Editor for inclusion in the next issue.

Nanotechnology

Synthesis and use of targeted radiation enhancing iron oxide-silica-gold nanoshells for imaging and treatment of cancer

Magnetic iron oxide nanoparticles (MIONs) having silica (SiMION) and gold-silica (AuSiMION) nanoshells, methods of their preparation, and their use in cancer imaging and therapy applications are disclosed by John Hopkins researchers (WO2015070036 (A1)).

Solid gold-nickel alloy nanoparticles and production method thereof

The purpose of the present invention, described my Japanese researchers, is to provide novel solid gold-nickel alloy nanoparticles and a production method thereof. Provided are solid gold-nickel alloy nanoparticles having a particle diameter of 500 nm or less. In particular, gold-nickel alloy nanoparticle are provided in which the concentration of nickel in the gold-nickel alloy is 2.0–92.7 wt%, and the main component is a gold-nickel alloy in which gold and nickel are in a nano-level fine mixed state. The gold-nickel alloy particles have as the main component a substitutional solid solution of gold and nickel. These gold-nickel alloy particles are optimally formed by mixing and discharging gold ions, and a substance having reducing characteristics in the thin film fluid occurring between processing surfaces which are arranged facing each other, which can move towards and away from each other, and at least one of which rotates relative to the other (US2015098858 (A1)).

The synthesis of core-shell metal semiconductor nanomaterials

South African researchers present a solution-based route to biocompatible, cysteine-capped gold-zinc telluride (Au-ZnTe) core/shell nanoparticles with potential in biomedical applications. The optical properties of the core/shell nanoparticles show no features of the individual parent components. The tunable emission properties of the semiconductor shell render the system useful for imaging and biological labelling applications (WO2015019297 (A1)).

Inherently stealthy and highly tumor-selective gold nanoraspberries for photothermal cancer therapy

Owing to their unique optical properties such as large absorption and scattering cross section and large enhancement of electromagnetic field at the surface, plasmonic nanostructures have received extensive attention as a highly promising class of materials for nano-oncology. Most of the existing plasmonic nanostructures require extensive post-synthesis treatments and biofunctionalization routines to mitigate their cytotoxicity and/or make them tumor-specific. Here, US-based researchers report one-pot synthesis of a novel class of plasmonic nanostructures, namely, gold nanoraspberries (GRBs) with tunable size and localized surface plasmon resonance by using a naturally abundant polysaccharide, chitosan, which acts as a template and capping agent (Ghandra et al., Scientific Reports, 5, Article number: 10311. doi:10.1038/srep10311). Significantly, the GRBs, which do not require any further biofunctionalization, exhibit excellent selectivity to tumor

cells, thus enabling locoregional therapy at the cellular level. We demonstrate the tumor-selectivity of GRBs by photothermal ablation of tumor cells selectively from their co-culture with normal cells. The simple, scalable, and tumor-selective nature of GRBs makes them excellent candidates for translational plasmonics-based nanomedicine.

Gold nanoparticle-enabled blood test for early stage cancer detection and risk assessment

When citrate ligands-capped gold nanoparticles are mixed with blood sera, a protein corona is formed on the nanoparticle surface due to the adsorption of various proteins in the blood to the nanoparticles. Using a two-step gold nanoparticle-enabled dynamic light scattering assay, Zheng et al. (ACS Appl Mater Interfaces. 2015 Apr 1;7(12):6819–27. doi: 10.1021/acsami.5b00371) discovered that the amount of human immunoglobulin G (IgG) in the gold nanoparticle protein corona is increased in prostate cancer patients compared to noncancer controls. Two pilot studies conducted on blood serum samples collected at Florida Hospital and obtained from Prostate Cancer Biorespository Network (PCBN) revealed that the test has a 90–95 % specificity and 50 % sensitivity in detecting early stage prostate cancer, representing a significant improvement over the current PSA test. The increased amount of human IgG found in the protein corona is believed to be associated with the autoantibodies produced in cancer patients as part of the immunodefense against tumor. Proteomic analysis of the nanoparticle protein corona revealed molecular profile differences between cancer and noncancer serum samples. Autoantibodies and natural antibodies produced in cancer patients in response to tumorigenesis have been found and detected in the blood of many cancer types. The test may be applicable for early detection and risk assessment of a broad spectrum of cancer. This new blood test is simple, low cost, requires only a few drops of blood sample, and the results are obtained within minutes. The test is well suited for screening purpose. More extensive studies are being conducted to further evaluate and validate the clinical potential of the new test.

Nanocomposites of gold Nanoparticles@Molecularly imprinted polymers: Chemistry, processing, and applications in sensors

Gold nanoparticles (AuNPs) have stimulated a wide range of interest these past years due to their remarkable optical, electronic, and catalytic properties. Generally, the use of these nanoparticles requires their functionalization or combination with functional molecules, the nature of which depends on the target application. Among the numerous possibilities offered by chemistry, some recent papers report the coupling of AuNPs with molecularly imprinted polymers (MIPs) for the design of plasmonic-based AuNPs@MIP sensors. In such systems, a target analyte can be captured from a complex medium with a high specificity and selectivity owing to the exceptional chemical properties of the MIP matrix while the recognition event can be translated into a measurable physical signal (optical, electric, and piezoelectric), the enhancement of which can be mediated by AuNPs. Despite such unique and intriguing advantages of AuNPs@MIP nanocomposites, there are still only limited numbers of studies regarding this field at the interface between plasmonics and functional polymers. This review focuses on the chemistry, processing, and applications of these nanohybrid materials, especially in the field of highly sensitive sensors. A prospect for the exploration of novel multicomposites combining AuNPs@MIPs with other kinds of nanoparticles (such as carbon nanotubes, graphene, and TiO_2) is provided in this review by French researchers, with original strategies to optimize the functionality and sensitivity of these nanocomposites-based sensors (Ahmad et al., Chem. Mater., Article ASAP, DOI: 10.1021/acs.chemmater.5b00138).

Gold nanoshell-decorated silicone surfaces for the near-infrared (NIR) photothermal destruction of the pathogenic bacterium *E. Faecalis*

Catheter-related infections (CRIs) are associated with the formation of pathogenic biofilms on the surfaces of silicone catheters, which are ubiquitous in medicine. These biofilms provide protection against antimicrobial agents and facilitate the development of bacterial resistance to antibiotics. The application of photothermal agents on catheter surfaces is an innovative approach to overcoming biofilm-generated CRIs. Gold nanoshells (AuNSs) represent a promising photothermal tool, because they can be used to generate heat upon exposure to near-infrared (NIR) radiation, are biologically inert at physiological temperatures and can be engineered for the photothermal ablation of cells and tissue. In this study, AuNSs functionalized with carboxylate-terminated organosulfur ligands were attached to model catheter surfaces and tested for their effectiveness at killing adhered *Enterococcus faecalis* (*E. faecalis*) bacteria (Khantamat et al., ACS Appl. Mater. Interfaces, 2015, 7 (7), pp 3981–3993. DOI: 10.1021/am506516r. The morphology of the AuNSs was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), while the elemental composition was characterized by energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Furthermore, optical and photothermal properties were acquired by ultraviolet–visible (UV–vis) spectroscopy and thermographic imaging with an infrared camera, respectively. Bacterial survival studies on AuNS-modified surfaces irradiated with and without NIR light were evaluated using a colony-formation assay. These studies demonstrated that

AuNS-modified surfaces, when illuminated with NIR light, can effectively kill *E. faecalis* on silicone surfaces.

Gold nanoparticle-loaded filter paper: a recyclable dip-catalyst for real-time reaction monitoring by surface enhanced Raman scattering

Spanish researchers report a robust and recyclable 'dip-catalyst' based on a gold nanoparticle (Au NP)-loaded filter paper composite, prepared by a simple dip-coating process using concentrated Au NP suspensions in toluene (Zheng et al., Chem. Commun., 2015, 51, 4572–4575. DOI: 10.1039/C4CC09466B). While acting as catalysts, the composites display excellent surface enhanced Raman scattering (SERS) efficiency, allowing the real-time monitoring of chemical reactions.

Electronics

Refractory metal barrier in semiconductor devices

US-based Skyworks Solutions researchers describe gate metallization structures and methods for semiconductor devices, wherein a refractory metal barrier is implemented to provide performance improvements. Transistor devices are disclosed having a compound semiconductor substrate and an electron-beam evaporated gate structure including a layer of tantalum nitride (TaNx), a layer of titanium (Ti), and a layer of gold (Au) (US2015123169 (A1)).

Paper-supported nanostructured ultrathin gold film electrodes—Characterization and functionalization

Finnish researchers fabricated ultrathin gold films (UTGFs) on a nanostructured latex-coated paper substrate by physical vapour deposition (PVD) with the aim to provide low-cost and flexible conductive electrodes in paper-based electronics (Ihalainen et al., Applied Surface Science, Volume 329, 28 February 2015, Pages 321–329). Morphological, electric and optical properties of UTGFs were dependent on the deposited film thickness. In addition, UTGFs were functionalized with insulating and hydrophobic 1-octadecanethiol self-assembled monolayer and inkjet-printed conductive and hydrophilic poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT–PSS) layer, and their electrochemical properties were examined. Results showed that sufficient mechanical stability and adhesion of UTGFs deposited on latex-coated paper were achieved without the need on any additional adhesive layers, enabling a more robust fabrication process of the electrodes. UTGF electrodes tolerated extensive bending without adverse effects and conductivity comparable to the bulk gold was obtained already with the film thickness of 6 nm. Although not been fabricated with the high-throughput method like printing, a very low material consumption (~12 $\mu g/cm^2$) together with a high conductivity (resistivity $<3\times10^{-6}$ Ω cm) makes the UTGFs electrodes potential candidates low-cost components in flexible electronics. In addition, the excellent stability of the UTGF electrodes in electrochemical experiments enables their application in the development of paper-based electrochemical platforms, e.g., for biosensing purposes.

Gold-functionalized graphene as conductive filler in UV-curable epoxy resin

Graphene sheets (GNPs) were functionalized with gold nanoparticles via a spontaneous deposition of gold particles on its surface occurred by chemical reduction of (Au^{3+}) as reported by Martin-Gallego et al. (Journal of Materials Science, January 2015, Volume 50, Issue 2, pp 605–610. Even after only 1 min of reaction, the reduction of Au^{3+} into metallic Au^0 takes place in evidencing the rapid and spontaneous character of the reduction. The particles, after only 3 min of deposition, have very small diameters, with average centred at 17 nm. The Au–GNP nanofillers were dispersed into UV-curable epoxy resin. Conductivity of the epoxy crosslinked samples containing Au–GNP nanofiller was compared to the values obtained for epoxy nanocomposite containing the same amount of bare graphene; the electrical conductivity was significantly increased by the addition of Au–GNP nanofiller, of about four orders of magnitude. This could be attributed to a charge transfer mechanism, which is strongly enhanced by the presence of gold NPs.

Fuel cell/battery technologies

Separator for fuel cells, fuel cell, fuel cell stack and method of manufacturing separator for fuel cells

Japanese researchers describe a separator for fuel cells. The separator includes a base material; an underlying alloy layer formed on the base material; and a gold plate layer formed on the underlying alloy layer. The separator is characterized in that the underlying alloy layer is formed of an M1-M2-M3 alloy (where M1 is at least one element selected from Ni, Fe, Co, Cu, Zn, and Sn, M2 is at least one element selected from Pd, Re, Pt, Rh, Ag, and Ru, and M3 is at least one element selected from P and B) (US2015125777 (A1)).

Au-coated carbon electrodes for aprotic Li–O_2 batteries with extended cycle life: the key issue of the Li-ion source

Despite having the capability of achieving high energy densities, Li–O_2 batteries still suffer from many inherent

disadvantages such as electrolyte stability, sluggish kinetics of the oxygen reduction/evolution reactions in the aprotic environment and electrodes stability.

German researchers have demonstrated that, by combining electrochemical and analytical techniques, the performances of Li–O_2 batteries based on LiTFSI-Tetraglyme electrolyte and Au-coated carbon electrodes are manly hindered by the instability of the lithium metal anode in the oxygen-saturated environment (Balasubramanian et al., Journal of Power Sources, Volume 278, 15 March 2015, Pages 156–162). Although the Au-coated carbon electrodes are able to minimize side reactions arising from electrolyte decomposition, oxygen crossover on the lithium metal results in the formation of decomposition products (LiOH and Li_2CO_3) that are clearly detrimental for the battery performance. Finally, it is demonstrated that the Au-coated carbon electrodes in combination with the LiTFSI-Tetraglyme electrolyte can sustain extended cycling (100 cycles) when a more stable source of Li-ion, namely lithium iron phosphate (LFP), is used.

A high-performance direct formate-peroxide fuel cell with palladium–gold alloy coated foam electrodes

Reported is a new type of direct formate fuel cell (DFFC) coupling an alkaline formate anode with an acid peroxide cathode (DFPFC), and its theoretical cell voltage reaches as high as 2.83 V (Li et al., Journal of Power Sources. Volume 278, 15 March 2015, Pages 569–573). A proof-of-concept experimental study indicates that when using the as-proposed spontaneous-deposited PdAu foam electrodes, the DFPFC can yield an open-circuit voltage of 1.51 V and a peak power density of 331 mW cm^{-2} at 60 °C, which are higher than the state-of-the-art anion-exchange membrane DFFC.

Catalysis

Reversible bifunctional air electrode catalyst

US researchers disclose a catalyst for the two electron reduction of oxygen. The catalyst can be reversible or near-reversible. The catalyst comprises a gold and a cobalt coordination complex, i.e., N,N'-bis(salicylidene)ethylenediaminocobalt (II) (cobalt salen) or a derivative thereof. The cobalt coordination complex can be polymerized to form a film, for example, via electropolymerization, to cover a gold surface. Also provided are metal-air batteries, fuel cells, and air electrodes that comprise the catalyst, as well as methods of using the catalyst, for example, to reduce oxygen and/or produce hydrogen peroxide (WO2015066630 (A1)).

Method for electrocatalytic reduction using Au nanoparticles tuned or optimised for reduction of CO_2 to CO

Selective electrocatalytic reduction of carbon dioxide (CO2) to carbon monoxide (CO) on gold (Au) nanoparticles (NPs) in 0.5 M KHCO3 at 25 DEG C is described by scientists at Brown University. Among monodisperse 4-, 6-, 8-, and 10-nm NPs tested, the 8 nm Au NPs show the maximum Faradaic efficiency (FE), up to 90 % at −0.67 V vs. reversible hydrogen electrode. Density functional theory (DFT) calculations suggest that edge sites dominate over corner sites on the Au NP surface facilitating stabilization of the reduction intermediates, such as COOH*, and the formation of CO. This mechanism is further supported by the fact that Au NPs embedded in a matrix of butyl-3 methylimidazolium hexafluorophosphate for more efficient COOH* stabilization exhibit even higher reaction activity (3 A/g mass activity) and selectivity (97 % FE) at −0.52 V (vs. RHE). Use of monodisperse Au NPs to optimize the available reaction intermediate binding sites thus allows efficient and selective electrocatalytic reduction of CO2 to CO (WO2015057917 (A1)).

Catalytic oxidation of uronic acids to aldaric acids

Dutch researchers disclose the oxidation of uronic acids, such as galacturonic acid, to the corresponding aldaric acids (characterized by the formula HOOC-(CHOH)n-COOH, with n being an integer of from 1 to 5) such as galactaric acids. The starting material comprising the uronic acid is subjected to oxygen under the influence of a supported gold catalyst and in the presence of a base. The oxidation occurs in good selectivity and yield, under unexpectedly mild conditions. A source of galacturonic acids is pectin, such as that derived from sugar beet pulp.

Effect of Au nano-particle aggregation on the deactivation of the $AuCl_3$/AC catalyst for acetylene hydrochlorination

A detailed study of the valence state and distribution of the $AuCl_3$/AC catalyst during the acetylene hydrochlorination deactivation process is described and discussed by Chinese researchers (Dai et al., Scientific Reports, 5, Article number: 10553. doi: 10.1038/srep10553). Temperature-programed reduction and X-ray photoelectron spectral analysis indicate that the active Au^{3+} reduction to metallic Au^0 is one reason for the deactivation of $AuCl_3$/AC catalyst. Transmission electron microscopy characterization demonstrated that the particle size of Au nano-particles increases with increasing reaction time. The results indicated that metallic Au^0 exhibits considerable catalytic activity and that Au nano-particle aggregation may be another reason for the $AuCl_3$/AC catalytic activity in acetylene hydrochlorination.

Ozone-activated nanoporous gold: a stable and storable material for catalytic oxidation

Research from Cynthia Friend's lab describes a new method for facile and reproducible activation of nanoporous gold (npAu) materials of different forms for the catalytic selective partial oxidation of alcohols under ambient pressure, steady flow conditions (Personick et al., ACS Catal., Just Accepted Manuscript, DOI: 10.1021/acscatal.5b00330). This method, based on the surface cleaning of npAu ingots with ozone to remove carbon documented in ultrahigh vacuum conditions, produces active npAu catalysts from ingots, foils, and shells by flowing an ozone/dioxygen mixture over the catalyst at 150 °C, followed by a temperature ramp from 50 to 150 °C in a flowing stream of 10 % methanol and 20 % oxygen. With this treatment, all three materials (ingots, foils, and shells) can be reproducibly activated, despite potential carbonaceous poisons resulting from their synthesis, and are highly active for the selective oxidation of primary alcohols over prolonged periods of time. The npAu materials activated in this manner exhibit catalytic behavior substantially different from those activated under different conditions previously reported. Once activated in this manner, they can be stored and easily reactivated by flow of reactant gases at 150 °C for a few hours. They possess improved selectivity for the coupling of higher alcohols, such as 1-butanol, and are not active for carbon monoxide oxidation. This ozone-treated npAu is a functionally new catalytic material

New catalyst series from the Sol–Gel-entrapment of gold nanoparticles in organically modified silica matrices: proof of performance in a model oxidation reaction

Gold nanoparticles were sol–gel-entrapped in the mesoporous structure of organically modified silica matrices, and the resulting Silia*Cat* Au materials were tested as oxidation catalysts in the model reaction of 1-phenylethanol with hydrogen peroxide (Ciriminna et al., ChemCatChem, Volume 7, Issue 2, pages 254–260, January 2015). The new materials were characterized by electronic microscopy, IR spectroscopy, and cryogenic N_2 sorption. The results point to conclusions of general validity that allow us to advance towards the practical use of supported gold nanoparticles in a number of applications.

Increased co-oxidation activity for mercury under hot and cold site coal power plant conditions—Preparation and evaluation of Au/TiO_2-coated SCR-DeNO*x* catalysts

The investigation aimed to develop SCR-catalysts with enhanced oxidation activity for elemental mercury (Dranga & Koeser. Applied Catalysis B: Environmental, Volumes 166–167, May 2015, Pages 302–312). For this, different nano-sized TiO_2 particles were coated with 1 and 2 wt% gold. Suspensions obtained from these particles were used for dip-coating the commercial honeycomb-shaped V_2O_5–WO_3/TiO_2 reference SCR catalyst. The mercury oxidation activities of the Au/TiO_2-coated catalysts were investigated in the laboratory for the temperature range 180–390 °C and simulated coal-fuel flue gas conditions (O_2, SO_2, NO, H_2O, Hg, HCl, and without NH_3). At reaction temperatures from 180 to 320 °C, Au/TiO_2 coatings enhanced the mercury oxidation activity of the SCR catalyst significantly by a factor of 2. At higher reaction temperatures, the positive effect of the Au/TiO_2 coatings on mercury oxidation decreased and was strongly dependent on the HCl content of the flue gas. The impact of Au/TiO_2 coatings on the DeNOx activity of the SCR catalysts at 390 °C was only marginal. The measured SO_2/SO_3 conversion activity rates depended on the coating procedure and the gold content of the catalysts. In conclusion, the Au/TiO_2 coatings are promising for the development of multi-pollutant SCR-DeNOx catalysts with high mercury co-oxidation activity for cold-site configurations or flue gases with higher HCl contents.

Chemistry

Photovoltaic conversion element and photovoltaic cell

Hong Kong-based researchers describe organic photovoltaic (OPV) cells using gold complex(es) with as chemical structure of structure (I) as active material wherein R1-R15 are independently hydrogen, halogen, hydroxyl, an unsubstituted alkyl, a substituted alkyl, cycloalkyl, an unsubstituted aryl, a substituted aryl, acyl, alkoxy, acyloxy, amino, alkylamino, nitro, acylamino, aralkyl, cyano, carboxyl, thio, styryl, aminocarbonyl, carbamoyl, aryloxycarbonyl, phenoxycarbonyl, hydroxyalkyl, or an alkoxycarbonyl group. The OPV cell can be fabricated by thermal deposition or solution process such as spin coat and printing (WO2015043533 (A1)).

A novel aminotriazole-based NHC complex for the design of gold(I) anti-cancer agents: Synthesis and biological evaluation

A novel gold(I) complex based on an aminotriazole *N*-heterocylic carbene ligand represents a promising scaffold for the design of anticancer bioorganometallics. The complex triggered cytotoxic effects in HT-29 and MDA-MB-231 cancer cells, inhibited the activity of the enzyme thioredoxin reductase and showed an effective and fast cellular accumulation (Serebryanskaya et al., Med. Chem. Commun., 2015, Advance Article. DOI: 10.1039/C5MD00185D)

Coatings

Gold low-radiation coated glass and its manufacturing method

Scientists at Taiwan Glass Industry Corp describe an invention which provides a gold low-radiation coated glass and its manufacturing method, which is characterized in that the coated glass sequentially comprises a glass substrate, a underlying dielectric layer, a bottom barrier layer, a functional layer, a top barrier layer, a top dielectric layer, and a top metal layer, wherein the underlying dielectric layer is TiOx layer, the bottom barrier layer is NiCr layer or CrNx layer, the functional layer is Ag layer, the top barrier layer is NiCrNx layer or CrNx layer, the top dielectric layer is Si3N4 layer or ZnSnOx+ Si3N4 layer, and the top metal layer is Si layer. Accordingly, the gold low-radiation-coated glass of the present invention not only solves the phenomena that a general single-silver glass has no reflected light within 80 to 90°, and it also proposes a manufacturing method to plate a gold color by using non pure gold, so that the low-radiation-coated glass has beautiful, comfortable and affordable functions as a whole, which meet the need of the market (TW201502097 (A)).

Functional thin film coatings incorporating gold nanoparticles in a transparent conducting fluorine doped tin oxide matrix

Noble nanoparticle–metal oxide composites attract research interest due to their unique combination of properties. UK-based researchers report the successful combination of gold nanoparticles (AuNPs) and F-doped SnO_2 composites by layering, producing films that demonstrate unique and interesting optoelectronic properties–high visible transparency, electrical conductivity, and with additional plasmonic effects (Chew et al., J. Mater. Chem. C, 2015,3, 1118–1125, DOI: 10.1039/C4TC02275K). Both of the layers were deposited by aerosol-assisted chemical vapour deposition (AACVD) onto heated glass substrates. Four distinctive sets of films were prepared and analysed consisting of gold nanoparticles, F-doped SnO_2 (FTO), a layer of gold nanoparticles on FTO, and an FTO layer on gold nanoparticles. The sizes of the AuNPs were shown to depend on the precursor concentration used. Layered Au:FTO composite films have an attractive blue coloration from the surface plasmon resonance (SPR) of the AuNPs yet have high transparency in the visible region and are electrically conducting, comparable to commercial FTO.

Enhanced durability of gold-coated current collectors for high power electrochemical devices

A highly durable current collector by optimizing the Au electrochemical deposition conditions is reported by Korean researchers (Ryu at al., RSC Adv., 2015, 5, 43956–43960. DOI: 10.1039/C5RA07270K). The high corrosion resistance of the Au layers on the current collector is successfully modified by adjusting the applied current densities and utilizing pulse potentials. The optimized Au-coated current collector is evaluated as the electrode substrate portion of the electrochemical cell.